Determination of Optimum Conditions in Preparing Highly Reactive Electrogenerated Zinc by Gas Chromatograph

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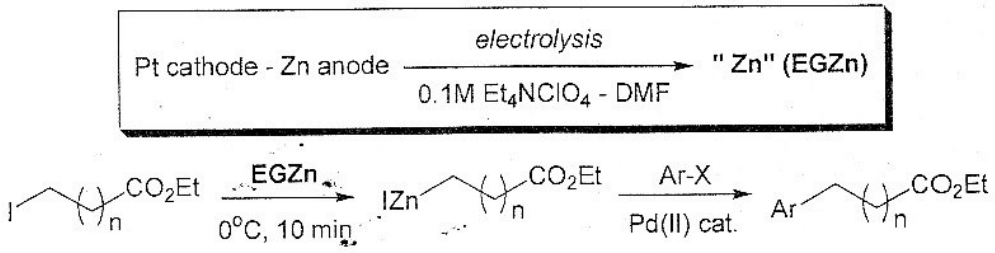
Abstract

Highly reactive electrogenerated zinc metal (EGZn/Naph) was readily prepared by electrolysis of a DMF solution containing naphthalene and a supporting electrolyte in a one-compartment cell fitted with a platinum cathode and a zinc anode. The reactivity of this EGZn/Naph was elucidated by an efficient transformation of ethyl 2-bromobutanoate as a model substrate into the corresponding organozinc compound, which can not be achieved by the use of usual zinc metal. It was found that the electrolysis at -10°C at a constant current of 60 mA/cm^2 under nitrogen atmosphere was the optimum conditions in preparing of the EGZn/Naph.

Keywords : optimum conditions, reactive zinc, organozinc compound, gas chromatography

Introduction

We have already reported a new method for the preparation of reactive zinc metal by electrolysis [1-3] and it used in isoprenylation [1] and allylation [2-4] of aldehydes and ketones. The authors also reported a facile preparation of organozinc compounds from functionalized alkyl iodides by using electrochemically generated reactive zinc (EGZn) and their cross-couplings with aryl halides (Scheme 1) [5].

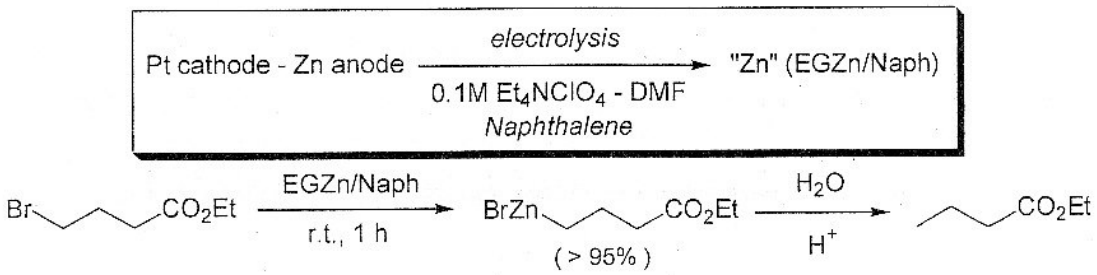


Scheme 1

However, no organozinc compounds have been obtained from alkyl bromides, even by the use of reactive EGZn. Recently, we developed a new electrochemical method for preparation of more highly reactive zinc (EGZn/Naph) by using naphthalene as a mediator. Such methods for preparing reactive zinc are very convenient and useful in organic synthesis. In this paper, we report an investigation to find out the optimum conditions in preparing EGZn/Naph.

Result and Discussion

Transformation of ethyl 4-bromobutanoate into the corresponding organozinc compound proceeded only in a 37% yield when EGZn was used. Yield of the transformation was monitored by GC and was determined by the disappearance of ethyl 4-bromobutanoate and also by the formation of protonated compound after hydrolysis of the organozinc bromide with diluted HCl solution. Therefore a new method for the preparation of more highly reactive zinc was desired in order to pursue more efficient transformation of organic bromides into the corresponding organozinc reagents. As a result of several attempts, highly reactive zinc metal EGZn/Naph was readily prepared by electrolysis of a DMF solution containing naphthalene and 0.1M Et_4NClO_4 in a one-compartment cell fitted with a platinum cathode and a zinc anode. Electrolysis at -10°C at a constant current of 60 mA/cm^2 in a nitrogen atmosphere was found to give EGZn/Naph with higher reactivity which could transform ethyl 4-bromobutanoate into the corresponding organozinc compound in almost quantitative yield (Scheme 2).



Scheme 2

Subsequent cross-coupling reaction of organozinc compound thus prepared with iodobenzene in the presence of 5 mol % $Pd((P(o\text{-}Tol)_3)_2)Cl_2$ catalyst at 70°C for 2 h gave the corresponding cross-coupling product, ethyl 4-phenylbutanoate in 97% isolated yield.

References

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